

Comment on “Four-component relativistic theory for NMR parameters: Unified formulation and numerical assessment of different approaches” [J. Chem. Phys. 130, 144102 (2009)]

Radosław Szmytkowski* and Patrycja Stefańska

Atomic Physics Division, Department of Atomic Physics and Luminescence,
Faculty of Applied Physics and Mathematics, Gdańsk University of Technology,
Narutowicza 11/12, 80–233 Gdańsk, Poland

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Abstract

In the paper commented on [J. Chem. Phys. 130 (2009) 144102], Cheng *et al.* derived a formula for the magnetic dipole shielding constant σ for the Dirac one-electron atom in its ground state. That formula involves an infinite series of ratios of the Euler’s gamma functions. We show that with some algebra the series may be expressed in terms of elementary functions. This leads to a simple closed-form expression for the shielding constant.

In a recent paper [1], Cheng *et al.* have discussed a four-component relativistic theory of NMR parameters. In particular, they have applied an analytical calculation technique, based on the Sturmian expansion of the first-order Dirac–Coulomb Green function, found some years ago by one of us in Ref. [2], to derive a formula for the magnetic dipole shielding constant σ for the Dirac one-electron atom in its ground state. They have shown that σ may be written in the form

$$\sigma = \sigma_{-1} + \sigma_{+2}, \quad (1)$$

where

$$\sigma_{-1} = -\frac{2Z\alpha^2}{9} \frac{2\gamma_1^2 + \gamma_1 - 4}{\gamma_1(2\gamma_1 - 1)} \quad (2)$$

and

$$\sigma_{+2} = \frac{2Z\alpha^2}{9} \frac{\Gamma(\gamma_2 + \gamma_1 - 1)\Gamma(\gamma_2 + \gamma_1 + 2)}{\Gamma(\gamma_2 - \gamma_1 - 1)\Gamma(\gamma_2 - \gamma_1 + 2)\Gamma(2\gamma_1 + 1)} \sum_{n=0}^{\infty} \frac{\Gamma(n + \gamma_2 - \gamma_1 - 1)\Gamma(n + \gamma_2 - \gamma_1 + 2)}{n!\Gamma(n + 2\gamma_2 + 1)(n + \gamma_2 - \gamma_1)}, \quad (3)$$

with

$$\gamma_\kappa = \sqrt{\kappa^2 - (\alpha Z)^2}. \quad (4)$$

Here Z is the nuclear charge, α is the Sommerfeld’s fine-structure constant, while $\Gamma(\zeta)$ is the Euler’s gamma function.

The representation of σ_{+2} displayed in Eq. (3) looks formidable. It is the purpose of this comment to prove that the series in Eq. (3) may be summed to a closed form, leading to an extremely simple expression for σ_{+2} .

*Corresponding author. Email: radek@mif.pg.gda.pl

To begin, we observe that with the aid of the well-known property $\zeta\Gamma(\zeta) = \Gamma(\zeta + 1)$, we may write

$$\Gamma(n + \gamma_2 - \gamma_1 + 2) = (n + \gamma_2 - \gamma_1)[\Gamma(n + \gamma_2 - \gamma_1) + \Gamma(n + \gamma_2 - \gamma_1 + 1)]. \quad (5)$$

Plugging Eq. (5) into Eq. (3) yields

$$\begin{aligned} \sigma_{+2} = & \frac{2Z\alpha^2}{9} \frac{\Gamma(\gamma_2 + \gamma_1 - 1)\Gamma(\gamma_2 + \gamma_1 + 2)}{\Gamma(\gamma_2 - \gamma_1 - 1)\Gamma(\gamma_2 - \gamma_1 + 2)\Gamma(2\gamma_1 + 1)} \\ & \times \left[\sum_{n=0}^{\infty} \frac{\Gamma(n + \gamma_2 - \gamma_1 - 1)\Gamma(n + \gamma_2 - \gamma_1)}{n!\Gamma(n + 2\gamma_2 + 1)} \right. \\ & \left. + \sum_{n=0}^{\infty} \frac{\Gamma(n + \gamma_2 - \gamma_1 - 1)\Gamma(n + \gamma_2 - \gamma_1 + 1)}{n!\Gamma(n + 2\gamma_2 + 1)} \right]. \end{aligned} \quad (6)$$

Since it is known [3, p. 36] that

$$\sum_{n=0}^{\infty} \frac{\Gamma(n + a_1)\Gamma(n + a_2)}{\Gamma(n + b)} \frac{z^n}{n!} = \frac{\Gamma(a_1)\Gamma(a_2)}{\Gamma(b)} {}_2F_1 \left(\begin{matrix} a_1, a_2 \\ b \end{matrix} ; z \right) \quad (|z| \leq 1), \quad (7)$$

where ${}_2F_1$ is the hypergeometric function, Eq. (6) may be cast into the form

$$\begin{aligned} \sigma_{+2} = & \frac{2Z\alpha^2}{9} \frac{\Gamma(\gamma_2 + \gamma_1 - 1)\Gamma(\gamma_2 + \gamma_1 + 2)}{(\gamma_2 - \gamma_1)(\gamma_2 - \gamma_1 + 1)\Gamma(2\gamma_1 + 1)\Gamma(2\gamma_2 + 1)} \\ & \times \left[{}_2F_1 \left(\begin{matrix} \gamma_2 - \gamma_1 - 1, \gamma_2 - \gamma_1 \\ 2\gamma_2 + 1 \end{matrix} ; 1 \right) + (\gamma_2 - \gamma_1) {}_2F_1 \left(\begin{matrix} \gamma_2 - \gamma_1 - 1, \gamma_2 - \gamma_1 + 1 \\ 2\gamma_2 + 1 \end{matrix} ; 1 \right) \right]. \end{aligned} \quad (8)$$

The following identity [3, p. 40]:

$${}_2F_1 \left(\begin{matrix} a_1, a_2 \\ b \end{matrix} ; 1 \right) = \frac{\Gamma(b)\Gamma(b - a_1 - a_2)}{\Gamma(b - a_1)\Gamma(b - a_2)} \quad [\text{Re}(b - a_1 - a_2) > 0] \quad (9)$$

is due to Gauss. Applying it to the two ${}_2F_1$ functions appearing in Eq. (8), we find

$${}_2F_1 \left(\begin{matrix} \gamma_2 - \gamma_1 - 1, \gamma_2 - \gamma_1 \\ 2\gamma_2 + 1 \end{matrix} ; 1 \right) = \frac{\Gamma(2\gamma_1 + 2)\Gamma(2\gamma_2 + 1)}{\Gamma(\gamma_2 + \gamma_1 + 1)\Gamma(\gamma_2 + \gamma_1 + 2)} \quad (10)$$

and

$${}_2F_1 \left(\begin{matrix} \gamma_2 - \gamma_1 - 1, \gamma_2 - \gamma_1 + 1 \\ 2\gamma_2 + 1 \end{matrix} ; 1 \right) = \frac{\Gamma(2\gamma_1 + 1)\Gamma(2\gamma_2 + 1)}{\Gamma(\gamma_2 + \gamma_1)\Gamma(\gamma_2 + \gamma_1 + 2)}. \quad (11)$$

Inserting Eqs. (10) and (11) into Eq. (8), after some rearrangements involving, among others, the identity

$$\gamma_2^2 = \gamma_1^2 + 3, \quad (12)$$

we eventually arrive at the following expression for σ_{+2} :

$$\sigma_{+2} = \frac{2Z\alpha^2}{27} \frac{\gamma_1 + 2}{\gamma_1 + 1}. \quad (13)$$

With no doubts, it looks much neater than the one in Eq. (3)!

Insertion of Eqs. (2) and (13) into Eq. (1) leads to the following closed-form representation of the magnetic dipole shielding constant for the relativistic hydrogen-like atom in its ground state:

$$\sigma = -\frac{2Z\alpha^2}{27} \frac{4\gamma_1^3 + 6\gamma_1^2 - 7\gamma_1 - 12}{\gamma_1(\gamma_1 + 1)(2\gamma_1 - 1)}, \quad (14)$$

which is identical with the expression found earlier by Moore [4], Pyper and Zhang [5] and Ivanov *et al.* [6] (after it is taken into account that the latter authors define σ with the opposite sign).

References

- [1] L. Cheng, Y. Xiao, W. Liu, J. Chem. Phys. 130 (2009) 144102
- [2] R. Szmytkowski, J. Phys. B 30 (1997) 825 [erratum: J. Phys. B 30 (1997) 2747; addendum: arXiv:physics/9902050]
- [3] W. Magnus, F. Oberhettinger, R. P. Soni, Formulas and Theorems for the Special Functions of Mathematical Physics, 3rd ed. (Springer, Berlin, 1966)
- [4] E. A. Moore, Mol. Phys. 97 (1999) 375
- [5] N. C. Pyper, Z. C. Zhang, Mol. Phys. 97 (1999) 391
- [6] V. G. Ivanov, S. G. Karshenboim, R. N. Lee, Phys. Rev. A 79 (2009) 012512 [preprint arXiv:0805.3424]